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We have measured the vertical profiles of several isotopomers of nitrous oxide, N_2O, in the stratosphere by balloon-borne infrared remote sensing between 15 and 35 km. In particular we distinguish the individual profiles and relative enrichments of the positional isotopomers $^{15}N^{14}N^{16}O$ and $^{14}N^{15}N^{16}O$ for the first time. We find a distinct and reproducible relative enrichment of the isotopomers which is in general agreement with measured photolysis rates in the laboratory and theoretical predictions. The results confirm photolysis as the dominant stratospheric loss process for N_2O and argue against suggestions that additional chemical sources of N_2O in the stratosphere are required to explain the observed heavy isotopic enrichments there.

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Vertical profiles of nitrous oxide isotopomer fractionation measured in the stratosphere

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Abstract. We have measured the vertical profiles of several isotopomers of nitrous oxide, N_2O, in the stratosphere by balloon-borne infrared remote sensing between 15 and 35 km. In particular we distinguish the individual profiles and relative enrichments of the positional isotopomers $^{15}N^{14}N^{16}O$ and $^{14}N^{15}N^{16}O$ for the first time. We find a distinct and reproducible relative enrichment of the isotopomers which is in general agreement with measured photolysis rates in the laboratory and theoretical predictions. The results confirm photolysis as the dominant stratospheric loss process for N_2O and argue against suggestions that additional chemical sources of N_2O in the stratosphere are required to explain the observed heavy isotopic enrichments there.

1. Introduction

Nitrous oxide (N_2O) plays two important roles in the atmosphere: it is the dominant source of nitrogen oxides active in stratospheric ozone depletion [*Crutzen*, 1970], and it is a major greenhouse gas [*IPCC*, 1996]. The conventional understanding of the global atmospheric budget of N_2O is that it is produced at the earth's surface by microbial nitrification and denitrification, destroyed in the stratosphere by UV photolysis, and has no atmospheric sources. It has a long lifetime of ca. 120 years and a global mean tropospheric mixing ratio of ca. 313ppbv that is increasing at ca. 0.2% per year, presumed due to human activity [*IPCC*, 1996]. However the full budget picture is not well resolved because of large uncertainties (up to 50%) in estimates of some individual source terms and an overall imbalance between best estimates of total sources and sinks [*Bouwman et al.*, 1995; *Kroeze et al.*, 1999]. Any attempt to resolve these budget uncertainties must also be constrained by the measured isotopic composition of atmospheric nitrous oxide and its sources and sinks [*Cliff and Thiemens*, 1997; *Dore et al.*, 1998; *Kim and Craig*, 1993; *McElroy and Jones*, 1996; *Naqvi et al.*, 1998; *Nevison et al.*, 1999; *Yoshida and Matsuo*, 1983]. N_2O in the lower stratosphere is isotopically heavy relative to tropospheric N_2O [*Kim and Craig*, 1993; *Moore*, 1974; *Rahn and Wahlen*, 1997], and its back diffusion to the troposphere has been postulated to balance the isotopically light biological sources in soils and oceans.

Two explanations for the origin of isotopically heavy stratospheric N_2O have been proposed. *Yung and Miller* [1997] presented a theoretical explanation based on isotopomer-dependent photolysis rates of N_2O which come about through small wavelength shifts in the UV absorption spectrum due to differences in the zero point vibrational energy of the different isotopomers. This theory predicts photolysis rates in the order 446 > 447 > 546 > 448 > 456 (446=$^{14}N^{14}N^{16}O$, 447=$^{14}N^{14}N^{17}O$, 546=$^{15}N^{14}N^{16}O$ etc.), which should leave the residual N_2O enriched in the heavier isotopes. In particular, the two ^{15}N isotopomers 456 and 546 should also have markedly different enrichment factors despite being of the same mass. The publication of this theory immediately spawned several independent laboratory studies of the isotopomeric enrichment factors at individual photolysis wavelengths, including the distinction of 456 and 546 isotopomers [*Rahn et al.*, 1998; *Roeckmann et al.*, 2000; *Turatti et al.*, 2000; *Zhang et al.*, 2000]. These studies confirmed the relative magnitudes of photolysis rates predicted by the theory, but in general obtained absolute enrichment factors about a factor of two larger [*Turatti et al.*, 2000].

An alternative explanation for isotopically heavy stratospheric N_2O is based on speculative atmospheric sources of N_2O from reactions of N_2 with excited O_3, O_2 or NO_2 molecules [*Estupinan et al.*, 2000; *McElroy and Jones*, 1996; *Prasad*, 1994; *Prasad*, 1997; *Zipf and Prasad*, 1998]. Such sources should produce N_2O with the 456 and 546 isotopomers in almost equal abundance, and thus the measurement of any enrichment of 456 relative to 546 is a key to distinguishing between these competing explanations. In this work we have measured individual vertical profiles and enrichment factors of the N_2O isotopomers 446, 456, 546 and 448 in the stratosphere by balloon-borne infrared remote sensing.

2. Experimental

Infrared spectroscopic techniques naturally distinguish the individual isotopomers of N_2O as different species and, given sufficient precision, provide a complementary approach to isotope ratio mass spectrometric (IRMS) methods conventionally used to determine ^{15}N and ^{18}O. In this work we have analyzed nine sets of solar infrared absorption spectra collected between 1992 and 1999 from Fort Sumner, New Mexico (34°N), Fairbanks, Alaska (65°N) and Esrange, Sweden (68°N). The spectra were collected with the Jet Propulsion Laboratory MkIV Fourier transform infrared spectrometer [*Toon*, 1991] from a balloon platform at 33-40 km altitude in solar occultation mode, in which the spectrum of the rising or setting sun is obtained through the limb of the

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earth's atmosphere. The spectra were analysed by least squares fitting of calculated spectra to the measured spectra in the ν_1 and ν_3 bands of N_2O near 1280 and 2200 cm^{-1} respectively. The spectral calculations and fitting were performed with the GFIT algorithm [*Goldman et al.*, 1999] using a 100 layer model atmosphere with new absorption line parameters provided by R.A. Toth for N_2O and HITRAN 1996 parameters [*Rothman et al.*, 1998] for other absorbing species. Each analysed spectrum provides the total slant column abundance of each isotopomer along the line of sight. For solar zenith angles greater than 90°, the measured slant column is heavily weighted to the atmospheric composition at the lowest (tangent) altitude of the line of sight because of the exponential fall-off in density with altitude and the curvature of the earth. During each occultation, spectra were typically acquired over a range of tangent altitudes from 10 to 40 km, at intervals of 1 to 4 km depending on latitude and season.

3. Results and Discussion

We measure isotopic fractionations in the conventional δ "per mil" scale where for example for the 456 isotopomer

$$\delta^{456} = (R_{456}(\text{sample}) / R_{456}(\text{reference}) - 1) \times 1000\ ‰$$

R_{456}(sample) is the ratio of the 456 to the 446 isotopomer slant column abundance and R_{456}(reference) is the corresponding ratio inherent in the line parameter database. In the conventional definition of δ, R is a ratio of local concentrations or mixing ratios rather than integrated slant column abundances. Because of the weighting of the slant columns to the tangent altitude, the slant column definition is a good approximation to the conventional δ at the tangent altitude. Figure 1(a) and (b) provides an overview of the fractionations plotted as the mean $\delta^{15}N=(\delta^{546}+\delta^{456})/2$ and difference $\delta^{546}-\delta^{456}$ versus tangent altitude for all nine balloon flights. The mean fractionation increases and the difference decreases by 50-100‰ with altitude up to 35 km. In the Esrange profile, measured inside the Arctic winter vortex under conditions of strong stratospheric subsidence, the fractionations change much more rapidly with altitude than in the other profiles measured outside the vortex. Above 30-35 km the scatter in the measurements increases in all profiles because there is less than 10% of the tropospheric N_2O amount remaining there and the relative measurement errors are high. Below 10-15 km there is also larger scatter because the atmosphere is virtually opaque and there is little solar intensity remaining in the spectral regions analysed.

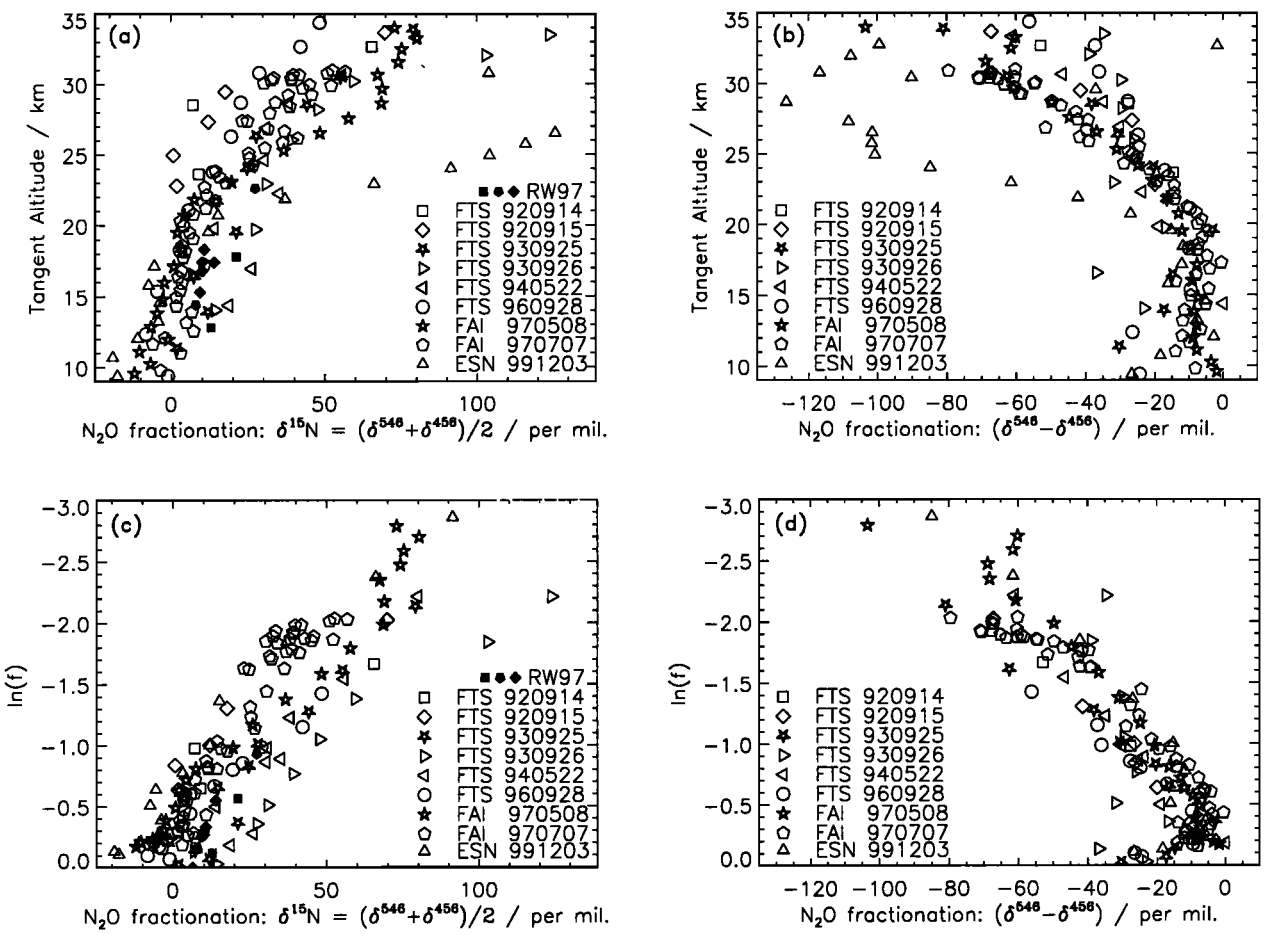

Figure 1. Vertical profiles of $\delta^{15}N=(\delta^{546} + \delta^{456})/2$ and $\delta^{546} - \delta^{456}$ of N_2O calculated from slant column abundances at each tangent altitude. Flight dates and locations are given in the legend: FTS = Fort Sumner (34°N), FAI = Fairbanks (65°N), ESN = Esrange (68°N), the 6-digit code is the date in yymmdd format. Panels (a) and (b) show the fractionations as a function of tangent altitude, and (c) and (d) as a function of *ln(f)*, the logarithm of the fraction *f* of N_2O in the slant column relative to the tropospheric value. Panels (a) and (c) also include the data of *Rahn and Wahlen*[1997] (solid symbols, diamonds = aircraft, pentagons = balloon data) and *Kim and Craig*[1993] (solid squares).

If the vertical profiles are determined only by photolysis, fractionation should be a Rayleigh distillation process [*Rahn and Wahlen*, 1997]. In this case the observed isotopic ratio R for any isotopomer relative to 446 at any altitude should be related to the fraction f of N_2O at that altitude relative to the unphotolyzed amount in the troposphere by

$$R = R_0 f^{\alpha-1}$$

and to a good approximation by

$$\delta = \delta_0 + \varepsilon.ln(f)$$

where R and δ have their usual definitions for each isotopomer, R_0 and δ_0 are the values of R and δ in the troposphere, α is the ratio of the individual isotopomer photolysis rates, and $\varepsilon = (\alpha-1) \times 1000$ is the relative enrichment factor (per mil). Plots of δ against $ln(f)$, if linear, provide apparent enrichment factors ε which can be compared to theory and other measurements. Figure 1(c) and (d) shows the same data as in (a) and (b) replotted against $ln(f)$ instead of altitude. The data now lie about single straight lines, and all nine individual profiles show generally good linearity, especially for $ln(f)<-0.3$, (altitude > 20 km). In particular, the arctic Esrange profile is now consistent with the other profiles. Table 1 summarizes the mean slopes of all plots for $ln(f) > -2.3$ ($f > 0.1$, altitude < 35 km) for each of the isotopomers as well as for the mean $\delta^{15}N = (\delta^{546}+\delta^{456})/2$ and difference $\delta^{546}-\delta^{456}$.

Constant multiplicative errors in the determination of δ and f (such as line strengths and assumed tropospheric N_2O mixing ratio) affect only the intercept of the Rayleigh plots and not the derived enrichment factors ε, which are determined from the slopes. The measured enrichment factors will be sensitive to errors whose effect is not constant with altitude or absorption strength in the spectra, such as zero offsets, instrument line shapes, assumed pressure broadening coefficients and temperature profiles. We have carried out extensive sensitivity tests to these quantities which indicate that the absolute fractionations should be accurate to better than 5‰ for δ^{546}-δ^{456} and 10‰ for $\delta^{15}N$. There is significant variability in the slopes of the plots between vertical profiles as indicated by the standard deviations in Table 1, which we believe to be due to the effects of transport, as discussed further below.

The consistent linearity and slope of the δ vs $ln(f)$ plots for each isotopomer supports an irreversible Rayleigh distillation-type loss process, presumably photolysis, as the dominant cause of the isotopic fractionation. The measured enrichment factors, ε, are in qualitative agreement with the theory of Yung and Miller: they are in the correct order, and their relative magnitudes agree within experimental error. However the absolute magnitudes are consistently around a factor of two larger than those predicted by Yung and Miller. They are however in good agreement with those measured in the laboratory for photolysis at 200-213nm, [*Rahn et al.*, 1998; *Roeckmann et al.*, 2000; *Turatti et al.*, 2000; *Zhang et al.*, 2000] which corresponds to the wavelength range of maximum solar photolysis [*Yung and Miller*, 1997]. Some simplifications in the original theory of Yung and Miller have been recognized [*Miller and Yung*, 2000; *Yung and Miller*, 1997; *Zhang et al.*, 2000], and inclusion of these in future calculations should clarify the quantitative discrepancy.

Table 1. Mean enrichment factors and standard deviations of N_2O isotopomers from nine vertical profiles. The enrichment factors for each flight are determined as the slopes of plots of δ vs $ln(f)$ by weighted least squares regression. Mean ^{15}N is the average of 456 and 546 isotopomers for comparison with mass spectrometric measurements.

	456	546	mean ^{15}N	546-456	448
Mean slope ε	-57.1	-27.3	-42.3	29.8	-42.6
Std deviation	9.5	13.5	10.1	11.5	29.4

Our measured enrichment factors of mean ^{15}N and ^{18}O (Table 1) are also significantly larger (i.e. more negative) than previous measurements from lower stratospheric samples reported by *Rahn and Wahlen* [1997], who found enrichment factors of -14.5‰ and -12.9‰ for mean ^{15}N and ^{18}O respectively for samples collected between 14.4 and 18.3 km altitude ($f > 0.6$). However these measurements are not irreconcilable. The individual data of Rahn and Wahlen are plotted (as solid symbols) in Figures 1(a) and (c), and can be seen to lie well within the range of our measurements. In the weighted least squares regressions our enrichment factors for each isotopomer (i.e. the regression slopes) are determined over an altitude range of approximately 15-30 km, with f values down to about 0.1. Below 20 km, ($f > 0.6$, $ln(f) \geq -0.5$ in Figure 1), the slopes of all δ vs. $ln(f)$ plots are much less well defined. A regression of our data only below 20 km, though less precise, would also lead to lower apparent enrichment factors more in agreement with those of Rahn and Wahlen. We also note that the enrichment factors calculated from Table 1 of Rahn and Wahlen for the higher altitude balloon data (14.4-22.6 km, solid pentagons) are significantly larger (e.g. -27‰ for ^{15}N) and in better agreement with our measurements. We believe the lower apparent enrichments measured at lower altitudes imply more transport and mixing of tropospheric air into the lower stratosphere. Such mixing will tend to dilute the photolytic enrichment of the heavy isotopomers with unphotolysed air and would explain the lower enrichments observed for a given f. Indeed, any variation of observed profiles from purely photolytically-determined profiles may provide a useful tracer for transport and mixing processes in the stratosphere.

4. Implications

Our results thus have important implications for global budget studies of N_2O. Several authors have used the previous data for the stratospheric isotopic composition [*Kim and Craig*, 1993; *Moore*, 1974; *Rahn and Wahlen*, 1997] to constrain the global isotopic N_2O budget [*Dore et al.*, 1998; *Kim and Craig*, 1993; *McElroy and Jones*, 1996; *Naqvi et al.*, 1998; *Nevison et al.*, 1999; *Yoshida and Matsuo*, 1983]. However our data suggest that the previous lower stratosphere fractionation measurements were in fact reduced by mixing, so that the true photolytic enrichment factors are actually significantly larger than was assumed. This implies that the modeled total return flux of N_2O to the troposphere would need to be smaller to achieve isotopic balance with the isotopically light biological sources at the earth's surface. This would in turn require larger surface sources to achieve the same total tropospheric N_2O burden. Further stratospheric measurements, combined with measurements of 546-456 differences in N_2O sources and tropospheric N_2O should improve our understanding of the global N_2O budget considerably.

These measurements also argue against the need to invoke novel chemical sources in the budget of N_2O in the stratosphere to explain its isotopically heavy signature [*McElroy and Jones*, 1996; *Prasad*, 1994; *Prasad*, 1997; *Zipf and Prasad*, 1998]. Although our observation of strong 546-456 fractionation does not strictly exclude the possibility that these novel sources play some role, the measured enrichment factors, their quantitative agreement with laboratory measurements, and their qualitative agreement with the theory of Yung and Miller suggest that differential isotopomeric photolysis rates provide a sufficient explanation for the observed isotopic composition of N_2O in the stratosphere.

Finally, we present actual atmospheric measurements of a new isotopic variable for N_2O studies, the positional asymmetry of ^{15}N fractionation, δ^{546}-δ^{456}. Like mass-independent fractionation [*Cliff and Thiemens*, 1997], the positional difference is a specific marker for a specific process (in this case photolysis), and should be a particularly valuable tracer in this respect. With the emergence of new analytical techniques for the determination of this isotopic signature [*Brenninkmeijer and Roeckmann*, 1999; *Esler et al.*, 2000; *Toyoda and Yoshida*, 1999], it should become a valuable addition to the isotopic toolbox. In a very recent paper published since acceptance of this work, *Yoshida and Toyoda* [2000] draw similar conclusions.

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